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Green light emission from the edges of organic single-crystal transistors

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We have fabricated ambipolar light-emitting field-effect transistors made of 1,4-bis(5-phenylthiophen-2-yl)benzene (AC5) single crystals, which have 35% fluorescent quantum efficiency. The obtained hole and electron mobilities were 2.9×10^{-1} $cm^2/V\,s$ and 6.7×10^{-3} $cm^2/V\,s$, respectively. These are the highest values among AC5 transistors. Importantly, although the light emission from the crystal surface was less than the detection level of the camera, we observed bright and polarized light emission from the edge of the single crystals. This polarized edge emission is attributed to the strong self-assembled light-confining nature and perfectly aligned transition dipole moments, which are advantageous for future laser devices. © *2010 American Institute of Physics*. [doi:10.1063/1.3504690]

Organic semiconductors have been investigated as the active layers in electronic and optoelectronic devices, including field-effect transistors (FETs), light-emitting diodes (LEDs), and photovoltaic cells, because of their potential application in plastic electronics.[1–3] In 2003, a different class of organic multifunctional devices was demonstrated called organic light-emitting field-effect transistors (LETs).[4] Although the reported tetracene LET was just a combination of light-emitting materials and unipolar FETs, the discovery of ambipolar LETs opened up possibilities for organic devices.[5–8]

Due to electrostatic carrier doping based on the capacitor structure of the transistors, ambipolar LETs can accumulate both holes and electrons simultaneously. As a result, this device realized a quasi p-i-n junction and possessed both the advantages of LEDs (excellent luminescent function) and FETs (high current capability). Therefore, ambipolar LETs provide a unique opportunity for investigating recombination physics in organic semiconductors as well as a route to current driven organic lasers. Since the electrically driven organic laser has not yet been realized in an organic LED structure, such an approach is very important.[9] In particular, the high carrier mobility of single crystals helps to increase the current density, which makes them one of the most promising structures for organic lasing devices.[8,10,11] However, the number of reported single-crystal ambipolar LETs is still limited.[8,10–14]

In this paper, we have fabricated ambipolar single-crystal LETs made of AC5 [Fig. 1(a)],[15] one of thiophene/phenylene co-oligomers (TPCOs). The single crystals of AC5 are characterized by good transport and outstanding optical properties, including laser oscillation and highly polarized emissions.[16–24] Most importantly, the reported internal fluorescent quantum efficiency of AC5 is extremely high (74% in solution and 100% as a single crystal).[25,26] The photoluminescent light is naturally confined within crystals and only the crystal fringes are strongly luminescent [Fig. 1(b)]. Consequently, in ambipolar LETs of AC5 single crystals, we observed well-polarized self-waveguided light emission from the crystal edge. This emission was due to the perfect alignment of transition dipole moments inside the crystals.

Recently, we have reported ambipolar single-crystal FETs based on several organic materials using polymethyl-

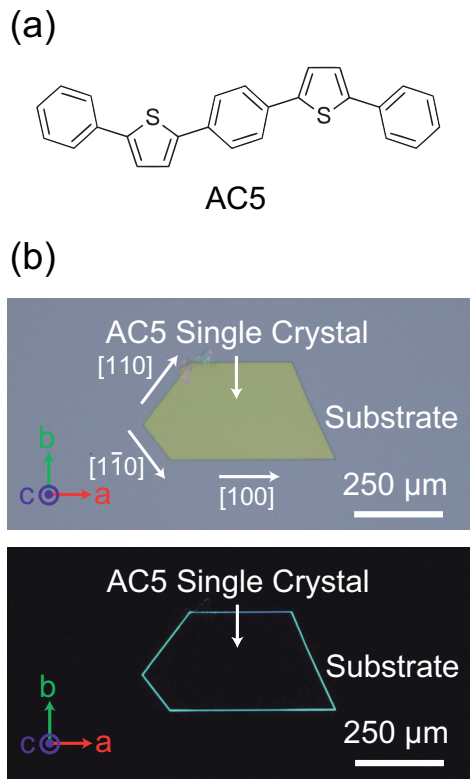

FIG. 1. (Color) (a) Chemical structure of an AC5 molecule. (b) Optical microscope images of an AC5 crystal under white-light (top) and under UV-light irradiation (bottom).

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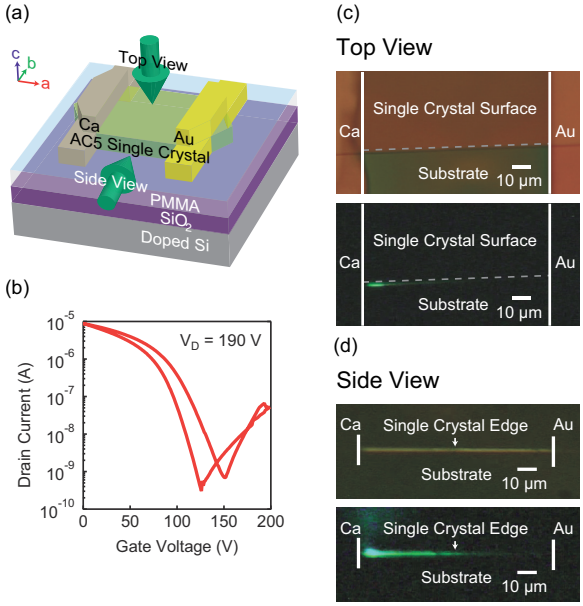

FIG. 2. (Color) (a) Schematic representation of an AC5 single-crystal transistor. (b) Transfer characteristics of an AC5 single-crystal transistor. (c) Top-view photographs of the AC5 single-crystal transistor under white light (top) and light emission from the transistor channel in the dark (bottom). (d) Side-view photographs of the AC5 single-crystal transistor under white light (top) and light emission from the transistor channel in the dark (bottom).

methacrylate (PMMA) as the gate dielectric to reduce the electron traps on the surface of the dielectric layer.[27,28] In the present study, we applied this method to AC5 crystals. The structure of the fabricated bottom-gate and top-contact FETs is schematized in Fig. 2(a). A highly doped silicon wafer with a 500 nm thermally grown SiO_2 layer was spin-coated with a 4 nm thick PMMA film using a toluene solution of PMMA. The films were maintained in an oven at 70 °C overnight and then at 100 °C for 3 h in a nitrogen atmosphere. Single crystals of AC5 were grown by physical vapor transport under an $Ar+H_2$ gas stream using a two zone furnace. We set the temperature to 260–270 °C as the high temperature molecular evaporation zone, and 220–230 °C as the low temperature single-crystal growth zone. The flow rate of Ar gas was around 50 ml/min. The typical dimensions of a grown AC5 single crystal were 5×5 mm^2. These crystals were transferred into a glove box without exposure to air and were laminated on the $PMMA/SiO_2/Si$ substrates using a technique described by Takahashi *et al.*[27] Au and Ca metal was thermally deposited on top of the AC5 crystals as source and drain electrodes, respectively, to reduce the injection barrier for both hole and electron carriers [Fig. 2(a)]. Electrical and optical characterization of the device was performed in the dark inside the glove box by means of a semiconducting parameter analyzer (Agilent E5270) and a charge-coupled device (CCD) camera (Olympus CS230B) attached to an optical microscope (Keyence VH-Z100R). The photoluminescent quantum efficiency was measured using an integrating sphere (C9920–2, Hamamatsu Co.) with a Xe lamp as an excitation light source.

We investigated the optical properties of our AC5 single crystals. As previously reported, single crystals of AC5 have optical confinement and self-waveguiding effects,[17,21,22] which are considered to partially account for their good light amplification properties. Our AC5 crystals also showed this reported light emission behavior. For instance, bright luminescence appeared at the sample edges and cracks [Fig. 1(b)]. In particular, compared with previous reports, fewer cracks were observed in our crystals. We detected a photoluminescent quantum efficiency of 35%, which is slightly higher than the previous result of $23\pm1\%$.[26] We also observed amplified spontaneous emission under ultraviolet laser excitation. These results strongly indicate that the quality of these crystals is higher than previous reports. Figure 2(b) plots the transfer characteristics of an AC5 single-crystal transistor. We routinely observed ambipolar transport in AC5 single crystal FETs using Au/Ca asymmetric electrodes and PMMA buffer layers. The maximum hole and electron mobilities from the saturation characteristics were 2.9×10^{-1} $cm^2/V\,s$ and 6.7×10^{-3} $cm^2/V\,s$, respectively. Both of these hole and electron mobilities are the highest values reported to date among the AC5 transistors,[19,20,23] suggesting high single-crystal quality and low contact resistance.

Next, we investigated the light-emitting properties of ambipolar AC5 single-crystal FETs. Figure 2(c) reveals the CCD images of an AC5 single-crystal device during ambipolar transistor operation. In the same manner as photoluminescence (PL) [Fig. 1(b)], strong light emission occurred solely at both edges of the AC5 crystal. The absence of surface emission is very similar to another single-crystal ambipolar TPCO LET, 5,5″-bis(4-biphenylyl)-2,2′:5′,2″-terthiophene (BP3T).[10] In addition, by varying the applied voltages, the position of the recombination/emission zone could be moved to any position along the channel. Figure 2(d) shows the side views of the device under ambipolar transistor operation. The details of the measurement set up have been reported already for BP3T LETs.[10] We have observed much brighter green emission from the edge of crystal LETs than from their surface. It also helped to measure optical spectra from AC5 LETs. The origin of this edge emission should be discussed.

We have collected PL and electroluminescence (EL) spectra from the same device to clarify the reason for this light-confinement [Fig. 3(a)]. These spectra are similar to each other and to the reported photoluminescent spectra.[16,26] Because the polarized PL spectra have been reported for AC5 crystals,[21] we have investigated the polarization character of the EL spectra from ambipolar AC5 LETs. The light emission was found to be strongly unidirectional and plane-polarized to the substrate [Fig. 3(b)]. The emission polarization ratio of the perpendicular to the parallel direction at the spectral peak (515 nm) was approximately 70. In BP3T LETs, such a polarization behavior is well explained by the alignment of transition dipole moments.[10] Similar analysis is necessary for AC5 LETs, to understand the observed polarized emission.

We have examined the molecular alignment of our single crystals. The crystal structure of thin AC5 single crystals were already investigated well by Yamao *et al.*[18] On the basis of the crystallographic data, we assign the crystal axes of our single crystals as in Fig. 1(b).[18,29] The numerical evaluations indicate that the crystal *c*-axis is almost perpendicular to the substrate (the angle between the crystal *c*-axis and a normal to the substrate is 0.7°). Consequently, we conclude that the emission is polarized along the *c*-axis. In BP3T single-crystal LETs, this emission corresponds to the transverse magnetic (TM) polarization, which is attributed to the upright transition dipole-moment direction.[10] Because the long molecular axis of AC5 molecules is almost parallel to the crystal *c*-axis,

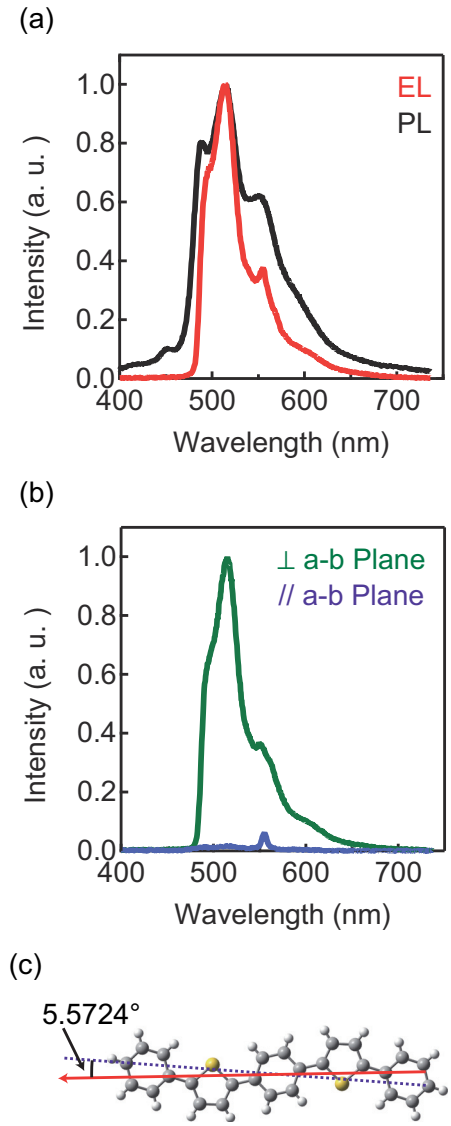

FIG. 3. (Color) (a) PL and EL spectra of an AC5 single-crystal transistor. (b) Optical polarization dependence of the EL spectra. (c) The transition dipole moment of AC5. Dashed line denotes the long molecular axes, and the red arrow indicates the transition dipole moment.

the similar situation to BP3T LETs is also expected in AC5 devices.

To determine the direction of the transition dipole moments more precisely, we have carried out theoretical calculations using the GAUSSIAN03 package. The geometry of the AC5 molecules was borrowed from the reported crystallographic data.[18,29] For the calculations, we used the single-excitation configuration interaction method with the correlation-consistent polarized valence double-zeta basis set. The results are represented in Fig. 3(c) as the red arrow. The obtained transition dipole moment is nearly parallel to the long molecular axes. The angle between the dipole moment and molecular axis is 5.6°, and the resulting angle between the dipole moment and a normal of the *ab*-plane is within 4.1°. Therefore, the EL emission from ambipolar AC5 LETs mainly corresponds to the TM polarization, owing to the upright alignment of the transition dipole moments. This confined TM-mode propagation is very similar to BP3T LETs.[10]

In conclusion, we have fabricated ambipolar LETs using AC5 single crystals, which have 35% external fluorescent quantum efficiency. The light emission from AC5 LETs was strongly confined inside the crystals and was mainly polarized along the crystal *c*-axis. This confined TM-mode propagation is well explained by the alignment of the transition dipole moments and might be advantageous for the realization of an organic laser.

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